Acta Cryst. (1995). **C51**, 1731–1732

Paraelastic $Pb_5Al_3F_{19}$ at 370 K

SABINE SARRAUTE AND JEAN RAVEZ

Laboratoire de Chimie du Solide, CNRS, Université Bordeaux I, 351 cours de la libération, 33405 Talence, France

GEORGE BRAVIC AND DANIEL CHASSEAU

Laboratoire de Cristallographie et de Physique Cristalline, CNRS ERS 133, Université Bordeaux I, 33405 Talence CEDEX, France

SIDNEY C. ABRAHAMS

Physics Department, Southern Oregon State College, Ashland OR 97520, USA

(*Received 24 October 1994; accepted 8 February 1995*)

Abstract

The paraelastic phase of lead aluminium fluoride, $Pb_5Al_3F_{19}$, forms above a transition temperature of about 360 K. The structure contains corner-sharing chains of AlF_6 octahedra, individual AlF_6 octahedra, individual F^- ions and Pb^{2+} ions. Both sets of independent AlF_6 octahedra are slightly distorted, with Al—F distances of 1.79 (3) and 1.80 (2) Å. The transition from the ferroelastic phase is weakly first order [Ravez, Andriamampianina, Simon, Rabardel, Ihringer & Abrahams (1994). *J. Appl. Cryst.* **27**, 362–368].

Comment

$Pb_5Al_3F_{19}$ has been reported to undergo three phase transitions on cooling from 400 to 80 K (Ravez, Andriamampianina, Simon, Rabardel, Ihringer & Abrahams, 1994). The structure of the antiferroelectric phase with space group *P*4/*n* at room temperature, together with structural changes that occur at the transition from the ferroelectric phase with space group *I*4*cm*, have been described previously (Andriamampianina, Gravereau, Ravez & Abrahams, 1994).

The phase-transition sequence in $Pb_5Al_3F_{19}$ is the following (with transition temperatures, on cooling):

$$\text{ferroelectric} \xleftarrow{120\text{ K}} \text{antiferroelectric} \xleftarrow{305\text{ K}} \text{ferroelastic} \xleftarrow{360\text{ K}} \text{paraelastic}$$

X-ray diffraction measurements have been made on a crystal, prepared by Ravez, Andriamampianina & Abrahams (1994), in the paraelastic phase at 370 K, using a heated flow of dry nitrogen gas. Absorption correction error was minimized by grinding the crystal to a sphere. The symmetry of the intensity distribution and the diffraction conditions $h + k + l = 2n$ lead to a choice of space groups *I*4, $I\bar{4}$ or *I*4/*m*.

Neither the pyroelectric p_3 nor the piezoelectric d_{33} coefficients have measurable magnitudes, suggesting that the point group is centrosymmetric. The two independent Al atoms occupy AlF_6 octahedra and the Pb atoms occupy tunnels of 2.5 Å radii.

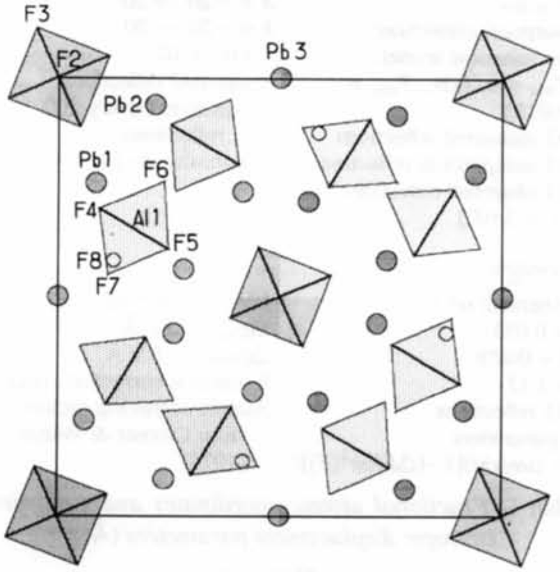

Fig. 1. Projection of the paraelastic phase of $Pb_5Al_3F_{19}$ along the *c* axis, with AlF_6 octahedra shown shaded. The larger filled circles represent Pb and the smaller open circles F8 atoms (see Table 1).

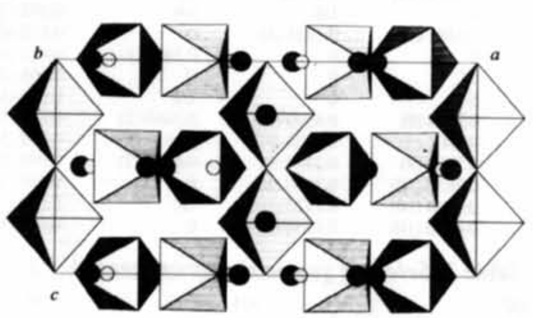

Fig. 2. Projection of the paraelastic phase of $Pb_5Al_3F_{19}$ along the *b* axis, with AlF_6 octahedra shown shaded. The larger filled circles represent Pb and the smaller open circles F8 atoms (see Table 1).

Experimental

The crystal was prepared by melting and slow cooling (Ravez, Andriamampianina & Abrahams, 1994). The density D_m was measured by flotation.

Crystal data

$Pb_5Al_3F_{19}$
$M_r = 1477.89$
Tetragonal
*I*4/*m*
$a = 14.285\ (7)$ Å
$c = 7.227\ (3)$ Å

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10$–26°
$\mu = 56.4\ \text{mm}^{-1}$

$V = 1475\,(3)$ Å^3
$Z = 4$
$D_x = 6.66$ Mg m^{-3}
$D_m = 6.66$ Mg m^{-3}

$T = 370$ K
Sphere
0.3 mm (radius)
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω/θ scans
Absorption correction: by spherical model
$T_{\min} = 0.0009$, $T_{\max} = 0.0185$
5787 measured reflections
1715 independent reflections
1314 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int} = 0.065$
$\theta_{\max} = 30°$
$h = -20 \rightarrow 20$
$k = -20 \rightarrow 20$
$l = 0 \rightarrow 10$
3 standard reflections monitored every 200 reflections intensity decay: <4%

Refinement

Refinement on F
$R = 0.053$
$wR = 0.058$
$S = 1.12$
1115 reflections
52 parameters
$w = (weight)[1-(\Delta F/6\sigma^2(F)]^2$

$(\Delta/\sigma)_{\max} = 0.01$
$\Delta\rho_{\max} = 5$ e Å^{-3}
$\Delta\rho_{\min} = -6$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from Cromer & Waber (1974)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Pb1	0.08474 (7)	−0.23970 (6)	0	0.018 (1)
Pb2	−0.06116 (6)	−0.21768 (5)	1/2	0.013 (2)
Pb3	0	1/2	1/4	0.072 (2)
Al1	0.1581 (4)	0.3255 (4)	0	0.012 (4)
Al2	0	0	0.2460 (1)	0.012 (4)
F1	0	0	0	0.038 (5)
F2	0	0	1/2	0.038 (5)
F3	0.3854 (9)	0.4500 (8)	0.2460 (2)	0.038 (5)
F4	0.2001 (9)	0.4076 (9)	0.1730 (2)	0.038 (5)
F5	0.3921 (9)	0.2494 (9)	0.6700 (2)	0.038 (5)
F6	0.2630 (10)	0.2610 (10)	0	0.038 (5)
F7	0.4530 (10)	0.1120 (10)	1/2	0.038 (5)
F8	0.4170 (10)	0.1250 (10)	0	0.038 (5)

Table 2. *Selected geometric parameters* (Å, °)

Pb1···F4$^{\rm i}$	2.52 (1)	Al1—F4$^{\rm xi}$	1.82 (1)
Pb1···F4$^{\rm ii}$	2.52 (1)	Al1—F5$^{\rm vii}$	1.78 (1)
Pb1···F6$^{\rm iii}$	2.54 (2)	Al1—F5$^{\rm xii}$	1.78 (1)
Pb2···F5$^{\rm iv}$	2.52 (1)	Al1—F6	1.75 (2)
Pb2···F5$^{\rm v}$	2.52 (1)	Al1—F7$^{\rm vii}$	1.81 (2)
Pb2···F6$^{\rm vi}$	2.54 (2)	Al2—F1	1.777 (8)
Pb2···F8$^{\rm vi}$	2.27 (2)	Al2—F2	1.836 (8)
Pb3···F7$^{\rm vii}$	2.51 (1)	Al2—F3$^{\rm vii}$	1.79 (1)
Pb3···F7$^{\rm viii}$	2.51 (1)	Al2—F3$^{\rm xiii}$	1.79 (1)
Pb3···F7$^{\rm ix}$	2.51 (1)	Al2—F3$^{\rm xiv}$	1.79 (1)
Pb3···F7$^{\rm x}$	2.51 (1)	Al2—F3$^{\rm i}$	1.79 (1)
Al1—F4	1.82 (1)		
F4$^{\rm i}$···Pb1···F4$^{\rm ii}$	139.7 (6)	F4—Al1—F5$^{\rm xii}$	92.7 (6)
F4$^{\rm ii}$···Pb1···F6$^{\rm iii}$	85.0 (3)	F5$^{\rm xii}$—Al1—F5$^{\rm vii}$	87.2 (9)
F5$^{\rm v}$···Pb2···F5$^{\rm iv}$	142.2 (6)	F4—Al1—F6	93.3 (6)
F5$^{\rm v}$···Pb2···F6$^{\rm vi}$	73.4 (3)	F4—Al1—F7$^{\rm vii}$	88.4 (6)
F5$^{\rm v}$···Pb2···F8$^{\rm vi}$	77.2 (6)	F5$^{\rm vii}$—Al1—F7$^{\rm vii}$	86.8 (6)
F6$^{\rm vi}$···Pb2···F8$^{\rm vi}$	75.2 (6)	F6—Al1—F7$^{\rm xii}$	177.7 (9)
F7$^{\rm vii}$···Pb3···F7$^{\rm viii}$	87.9 (6)	F1—Al2—F2	179.99
F7$^{\rm ix}$···Pb3···F7$^{\rm viii}$	121.2 (3)	F1—Al2—F3$^{\rm vii}$	92.0 (5)
F4—Al1$^{\rm xi}$—F4$^{\rm xi}$	87.0 (8)	F3$^{\rm i}$—Al2—F3$^{\rm vii}$	89.93 (3)
F4—Al1—F5$^{\rm vii}$	175.1 (7)	F3$^{\rm xiii}$—Al2—F3$^{\rm vii}$	176.1 (10)

Symmetry codes: (i) $\frac{1}{2}-y, x-\frac{1}{2}, \frac{1}{2}-z$; (ii) $\frac{1}{2}-y, x-\frac{1}{2}, z-\frac{1}{2}$; (iii) $y, -x, -z$; (iv) $x-\frac{1}{2}, y-\frac{1}{2}, \frac{3}{2}-z$; (v) $x-\frac{1}{2}, y-\frac{1}{2}, z-\frac{1}{2}$; (vi) $x-\frac{1}{2}, y-\frac{1}{2}, \frac{1}{2}+z$; (vii) $\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}-z$; (viii) $x-\frac{1}{2}, \frac{1}{2}+y, \frac{1}{2}-z$; (ix) $-y, x, z$; (x) $y, 1-x, 1-z$; (xi) $x, y, -z$; (xii) $\frac{1}{2}-x, \frac{1}{2}-y, z-\frac{1}{2}$; (xiii) $x-\frac{1}{2}, y-\frac{1}{2}, \frac{1}{2}-z$; (xiv) $y-\frac{1}{2}, \frac{1}{2}-x, \frac{1}{2}-z$.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: local program (unpublished). Program(s) used to refine structure: *CRYSTALS* (Watkin, Carruthers & Betteridge, 1985).

The authors wish to thank R. Von der Mühll for piezoelectric and pyroelectric tests and D. J. Watkin for providing the refinement program.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: DU1109). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Andriamampianina, V., Gravereau, P., Ravez, J. & Abrahams, S. C. (1994). *Acta Cryst.* **B50**, 135–141.

Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2A. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Ravez, J., Andriamampianina, V. & Abrahams, S. C. (1994). *Ferroelectrics*, **158**, 133–137.

Ravez, J., Andriamampianina, V., Simon, A., Rabardel, L., Ihringer, J. & Abrahams, S. C. (1994). *J. Appl. Cryst.* **27**, 362–368.

Watkin, D. J., Carruthers, J. R. & Betteridge, P. W. (1985). *CRYSTALS User Guide*. Chemical Crystallography Laboratory, Univ. of Oxford, England.

Acta Cryst. (1995). C51, 1732–1735

Octachlorosilasesquioxane, $Cl_8Si_8O_{12}$

KARL WILHELM TÖRNROOS

Structural Chemistry, Stockholm University,
106 91 Stockholm, Sweden

GION CALZAFERRI AND ROMAN IMHOF

Institute for Inorganic and Physical Chemistry,
University of Bern, Freiestrasse 3, CH-3000 Bern 9,
Switzerland

(*Received* 18 *December* 1994; *accepted* 27 *March* 1995)

Abstract

The structure of $Cl_8Si_8O_{12}$ is compared with those of the isostructural compounds $H_8Si_8O_{12}$ and $(CH_3)_8Si_8O_{12}$. The geometric deformations in $Cl_8Si_8O_{12}$ seem to